ISSN 0012-5008, Doklady Chemistry, 2018, Vol. 479, Part 1, pp. 31–35. © Pleiades Publishing, Ltd., 2018.
Original Russian Text © Z.V. Akhmetzyanova, G.R. Allakhverdili, A.S. Ovsyannikov, S.E. Solovieva, A.I. Konovalov, 2018, published in Doklady Akademii Nauk, 2018, Vol. 479, No. 2, pp. 149–153.

CHEMISTRY

Synthesis of New Photoswitchable Tectons Based on Thiacalix[4]arene Azo Derivatives in the 1,3-*Alternate* Conformation

Z. V. Akhmetzyanova[a], G. R. Allakhverdili[a], A. S. Ovsyannikov[a,b], S. E. Solovieva[a,b,*], and Academician A. I. Konovalov[a,b]

Received November 14, 2017

Abstract—The paper describes the first synthesis of molecular tectons, a series of ligands based on thiacalix[4]arenes in the 1,3-*alternate* stereoisomeric form containing photoswitchable azo groups in the side chain and carboxyl groups as potential binding sites for the synthesis of photoswitchable complexes and coordination polymers. In the case of *p-tert*-butylcalixarenes, the convergent approach is preferred.

DOI: 10.1134/S0012500818030023

The fabrication of so-called smart materials capable of reversible response to external stimuli (electromagnetic radiation, temperature and pH changes, moisture, deformation, and so on) for the use in modern technologies attracts great attention all over the world [1]. Among various types of external stimuli, resulting in morphological or structural changes of materials, light is one of the most simple and convenient one for use [2]. Therefore, the design of crystalline smart materials capable of photoswitching is a topical issue addressed by many scientists all over the world [3, 4].

Molecular tectonics is an effective approach to the design of crystalline materials possessing specified properties and formed by programmed molecular self-assembly of molecular tectons, that is, complementary molecular building blocks pre-organized in geometry and electronic structure. This approach can be used, in particular, to prepare metal-organic frameworks (MOFs), in which the adsorption/desorption of carbon dioxide molecules can be successfully controlled via photoswitching [5, 6]. At the same time, calixarene-based photoswitchable MOFs are still unknown. Owing to the possibility of spatial pre-organization and fine tuning of the calixarene macrocycle to a particular object (substrate), calixarene derivatives are widely used to fabricate supramolecular assemblies both in solution and in the crystalline phase [7–10]. In particular, upon the reaction with metal ions, they form either discrete or extended metal-organic structures [10, 11], which may serve for the manufacture of new functional materials.

In this study, with the aim of producing photoswitchable molecular frameworks, we designed and synthesized ligands — molecular tectons in the 1,3-*alternate* stereoisomeric form based on thiacalix[4]arenes. For this purpose, we introduced azo groups (–N=N–) into substituents in the lower rim of the macrocycle. On exposure to UV radiation, these groups undergo *cis–trans* isomerization and thus change the crystal structure and properties of the material. The azo groups were introduced in such a way that they were not involved in the metal-organic framework, but were located in the substituent side chain [6]. In this case, the photoswitching was not affected by steric factors preventing photoisomerization from the side of the metal-organic framework of the coordination polymer (Scheme 1a).

As coordinating groups, we chose carboxyl groups, as they are able to form strong coordination polymers with virtually any hard and soft (according to Pearson's principle) metal cations. We varied the mutual positions of the azo and carboxyl groups in order to obtain coordination polymers of different size (Scheme 1b). These macrocycles can also act as proton donors or acceptors in the formation of hydrogen-bonded molecular frameworks.

Two approaches were used for synthesis of thiacalix[4]arene azo derivatives in the 1,3-*alternate* conformation: divergent and convergent ones. In the divergent approach, the molecule is assembled starting from the center (calixarene platform) via successive

[a] *Kazan (Volga Region) Federal University, Kazan, 420008 Russia*
[b] *Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center, Russian Academy of Sciences, Kazan, 420029 Russia*
**e-mail: evgersol@yandex.ru*